ANNEX 5

TAINTING POTENTIAL OF ESTERS OF ALKANOLS AND MONOBASIC ALKANOIC ACIDS

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INTRODUCTION

Esters, at least the lower molecular weight esters, generally have strong, and often pleasant, odours. Esters of lower carbon number aliphatic alcohols and lower carbon number fatty acids contribute significantly to the characteristic odours of fruits, and others, for example methyl salicylate, contribute to the characteristic odours of fragrant plants. Because of their sensory properties, esters are likely to have the potential to taint fish, but only three of the 84 or so esters in the Composite List have been tested for this ability. This paper reviews the sensory properties of esters of alkanols and monobasic alkanoic acids as a subgroup of the esters in the Composite List, and discusses their potentials as tainting compounds for fish.

ESTERS IN THE EHS LIST

Esters are collected together in Chemical Class 10 in the EHS database. Within this group they are often further subdivided in printed comprehensive lists such as that in GESAMP Reports and Studies 35 into formates, acetates and acetoacetates, propionates and esters of higher molecular weight monobasic acids, acrylates and methacrylates, esters of hydroxy acids and dibasic aliphatic acids, and esters of aromatic dibasic acids including phthalates. There is very little data on sensory properties of esters other than those in the first three of these subgroups, esters of aliphatic monocarboxylic acids. The members of this subgroup in the Composite List, other than acetoacetates, acids with a carbon number greater than 5, and esters of unsaturated alcohols or acids are listed in Table 1. The names in the EHS list are used. The table shows the number of carbons in the alcohol and acid moieties of the ester, and the compounds are ranked by the number of carbons in the acid moiety. These esters are reviewed and discussed in this paper.

DATA ON TAINTING AND ON SENSORY PROPERTIES

Persson's (1984) comprehensive review of tainting by chemicals includes two esters - Amyl acetate and Ethyl acrylate, and I have not found any other data in the published literature. These two chemicals had been tested by Shumway and Palensky (1973) who reported that Amyl acetate did not taint trout exposed to 10 mg/l of the substance, the highest concentration tested, and that the tainting threshold of Ethyl acrylate was 0.06 mg/l. (Acrylates are not reviewed in this paper and are not listed in Table 1.) JETOC has provided information on tainting by Butyl butyrate which shows that it taints below 1 mg/l, and on the basis of this report the EHS Working Group has allocated a 'T' rating to Butyl butyrate and a '(T)' to Isobutyl butyrate.

There is a close association between tainting thresholds of chemicals and their detection thresholds in aqueous solutions, and the latter can be used as surrogates for the former. Data on detection thresholds of esters in water are available in the literature (Ahmed *et al*, 1978; Flath *et al*, 1967; Larsen and Poll, 1992; Powers and Quinlan 1973; Schnabel *et al*, 1988) and have been

collected in compilations, (Fazzalari, 1978; Van Gemert and Nettenbreijer, 1977). The paper by Schnabel *et al* (1988) is particularly important as the authors measured the detection thresholds of some 60 esters of alkanols and monobasic alkanoic acids.

Table 2 lists the odour detection thresholds in water of esters of the type under discussion obtained from these sources. Systematic chemical names are used here as they make clear the various isomers, and the compounds are ranked by the number of carbons in the acid contributing to the ester. For some esters there is more than one value in the literature and the geometric mean of these values have been listed. None of the sources of data give confidence limits for the measurements of the thresholds.

DISCUSSION

Inspection of Table 2 shows that almost all of the esters listed have odour detection thresholds at less than 1 mg/l. In the case of the lower molecular weight esters there is a trend for detection thresholds to decrease with increasing number of carbons in the acid moiety, and perhaps with increasing number of carbons in the alcohol moiety as well. The trend with carbon number in the acid moiety can be seen in Figure 1 which is a scatter plot of thresholds against carbon number in the acid. The different points shown at a particular carbon number represent various alcohol residues and various isomers of both the acid and alcohol moieties.

Odour detection thresholds decrease with increasing carbon number in the acid moiety up to C4 acids. Above that, the best that can be concluded is that they do not show a trend, up or down, with increasing carbon number. In a homologous series there is often a trend for detection thresholds to decrease with increasing carbon number in members of the series to a minimum, then increase. At sufficiently high molecular weights members of the series will be odourless. There is no indication of this increase of detection threshold with carbon number within the data set presented here, and no data could be found on esters above decanoates. There is an indication that ethyl esters have lower thresholds than methyl esters, but otherwise there is not a trend for thresholds to change systematically with carbon number in the alcohol moiety. The plot does not differentiate isomers of either the alcohol or the acid , but inspection of the data does not reveal a consistent effect on thresholds of branching in either the acid or the alcohol.

The ordinate of the graph is logarithm to the base 10 of detection thresholds in units of mg/l so the line at 0 is 1 mg/l, the limit used in the EHS hazard rating system for allocating 'T' ratings. The thresholds of all esters with acid carbon numbers of 3 or more are below this line, and those of all of the formates are above the line.

The acetates straddle the line and Figure 2 is a plot of detection thresholds of acetates against carbon number in the alcohol. Branched isomers are differentiated in this plot. Detection thresholds decrease with increasing size of the alcohol moiety up to C5, and thresholds of Methyl, Ethyl and Propyl, (C1-C3), acetates are above 1 mg/l. Thresholds increase slightly above this carbon number, but are below 1 mg/l, and mostly below 0.1 mg/l.

CONCLUSIONS

The data presented here do not support allocation of 'T' ratings to the formates presently in the Composite List. Detection thresholds of these formates decrease with increasing carbon number in the alcohol moiety, and it is possible that formates of higher molecular weight than butyl formates could have detection thresholds below the 1 mg/l limit. If any more formates are presented to the EHS Working Group for rating then the manufacturers should be required to provide at least threshold data, if not tainting data.

The data supports allocating 'T' ratings to esters of C3 and higher carbon number alkanoic acids up to C10, including all isomers. This range includes the propionates, butyrates and isobutyrates in the Composite List. The data from Japan on tainting by Butyl butyrate are consistent with this conclusion. Data on Propyl palmitate and Butyl stearate which are in the Composite List have note been found, or indeed on any palmitates or stearates. It is difficult to anticipate if these two chemicals have detection thresholds below 1 mg/l. The data set presented here goes only up to C10 acids, whose esters have detection thresholds around 0.01 mg/l, and it is possible that esters of palmitic, C16, and stearic, C18, acids are in that region of the homologous series where detection thresholds increase with increasing carbon number such that their detection thresholds could be above 1 mg/l.

The data do not support allocation of 'T' ratings to Methyl, Ethyl or Propyl acetates, but do support allocation to higher acetates. However Shumway and Palensky (1973) found that fish exposed to 10 mg/l of Amyl (C5) acetate did not acquire taint. Butyl butyrate, with a detection threshold in water of 0.19 mg/l, taints fish. Amyl acetate has a detection threshold in water of 0.012, an order lower than that of Butyl butyrate, and I would expect it to have a tainting threshold less than 1 mg/l. Despite the Shumway and Palensky result, my opinion is that Amyl acetate have a 'T' rating.

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Table 1: Esters of monohydric alcohols and monobasic acids in the EHS list

	carbon nos		hazard profile					
	alc.	acid	A	B	C	D	E	Remarks
Methyl formate	1	1	0	1	1	I	X	
Propyl formate	3	1	0	(0)	1	I	X	
Isobutyl formate	4	1	0	1	1	I	X	
Butyl formate	4	1	0	(1)	1	II	XX	
Methyl acetate	1	2	0	0	1	0	0	
Ethyl acetate	2	2	0	1	0	0	0	
Propyl acetate	3	2	0	1	0	0	0	
Isopropyl acetate	3	2	0	(1)	1	I	X	
sec-Butyl acetate	4	2	0	1	0	I	X	
Isobutyl acetate	4	2	0	2	1	I	X	
Butyl acetate	4	2	0	2	0	I	X	
Amyl acetate	5	2	0	2	0	0	X	Tested for tainting
sec-Amyl acetate	5	2	0	2	1	I	X	
Isoamyl acetate	5	2	0	2	0	I	X	
sec-Hexyl acetate	6	2	0	(2)	0	0	0	
Hexyl acetate	6	2	0	3	0	0	0	
Heptyl acetate	7	2	0	(3)	0	I	X	
Octyl acetate	8	2	0	2	1	I	X	
Methyl propionate	1	3	0	(1)	1	0	0	
Methyl butyrate	1	4	0	(2)	1	I	X	
Isobutyl isobutyrate	4	4	(T)	2	0	0	0	
Butyl butyrate	4	4	T	(2)	0	I	XX	Tested for tainting

Table 2: Detection thresholds of esters in aqueous solution

	carbon no.				carbon no.		
compound	alc.	acid	threshold mg/l	compound	alc.	acid	threshold mg/l
Methyl methanoate	1	1	306	Methyl butanoate	1	4	0.016
Ethyl methanoate	2	1	21.9	Methyl methylpropanoate	1	4	0.0019
Butyl methanoate	4	1	6.0	Ethyl butanoate	2	4	0.0012
Methyl ethanoate	1	2	8.3	Ethyl methylpropanoate	2	4	0.0001
Ethyl ethanoate	2	2	2.4	Propyl butanoate	3	4	0.0059
Propyl ethanoate	3	2	4.1	Propyl methylpropanoate	3	4	0.0002
2-Propyl ethanoate	3	2	2.8	Butyl butanoate	4	4	0.19
Butyl ethanoate	4	2	0.049	Methylpropyl methylpropanoate	4	4	0.040
Dimethylethyl ethanoate	4	2	0.19	Butyl methylpropanoate	4	4	0.12
Methylpropyl ethanoate	4	2	0.62	Pentyl methylpropanoate	5	4	0.060
Pentyl ethanoate	5	2	0.012	3-Methylbutyl methylpropanoate	5	4	0.19
2-Pentyl ethanoate	5	2	0.0028	Hexyl methylpropanoate	6	4	0.0095
3-Methylbutyl ethanoate	5	2	0.019	Methyl pentanoate	1	5	0.045
Hexyl ethanoate	6	2	0.014	Ethyl pentanoate	2	5	0.010
2-Heptyl ethanoate	7	2	0.19	Methylpropyl 2-methylbutanoate	4	5	0.060
Octyl ethanoate	8	2	0.024	Butyl 2-methylbutanoate	4	5	0.061
2-Ethylhexyl ethanoate	8	2	0.105	2-Butyl 2-methylbutanoate	4	5	0.061
Nonyl ethanoate	9	2	0.057	Pentyl pentanoate	5	5	0.039
Methyl propanoate	1	3	0.80	Pentyl 2-methylbutanoate	5	5	0.019
Ethyl propanoate	2	3	0.014	3-Methylbutyl 2-methylbutanoate	5	5	0.019
Propyl propanoate	3	3	0.19	Hexyl 2-methylbutanoate	6	5	0.19
Butyl propanoate	4	3	0.071	Methyl hexanoate	1	6	0.13
Dimethyethyl propanoate	4	3	0.019	Ethyl hexanoate	2	6	0.0019
3-Methylbutyl propanoate	5	3	0.019	2-Pentyl hexanoate	5	6	0.062
Hexyl propanoate	6	3	0.0080	Methyl heptanoate	1	7	0.0040
Heptyl propanoate	7	3	0.0040	Methyl octanoate	1	8	0.48
				Methyl decanoate	1	10	0.0061
				Ethyl decanoate	2	10	0.019

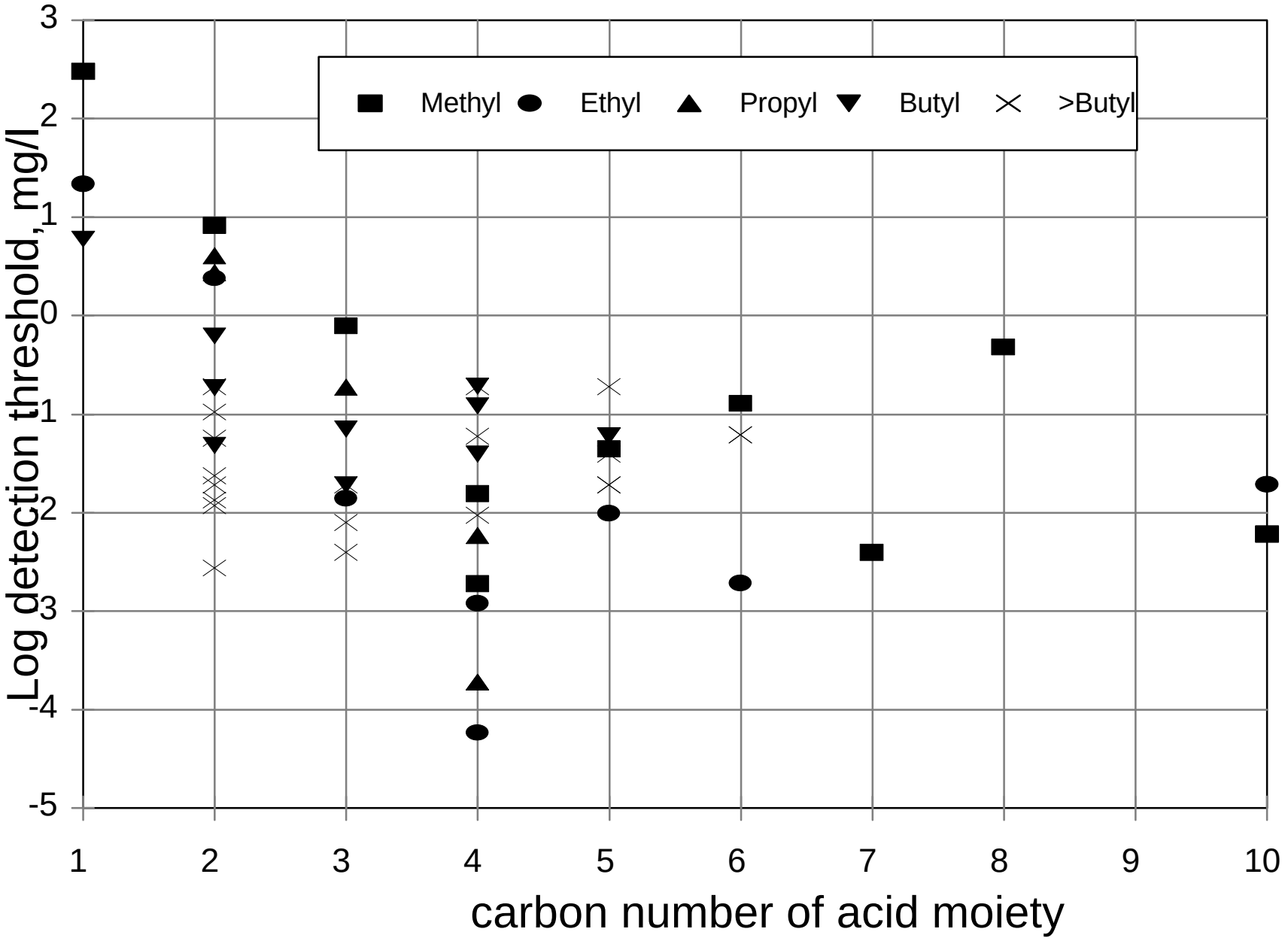

Figure 1. Odour detection thresholds of esters of alkanols and monobasic alkanoic acids, including isomers

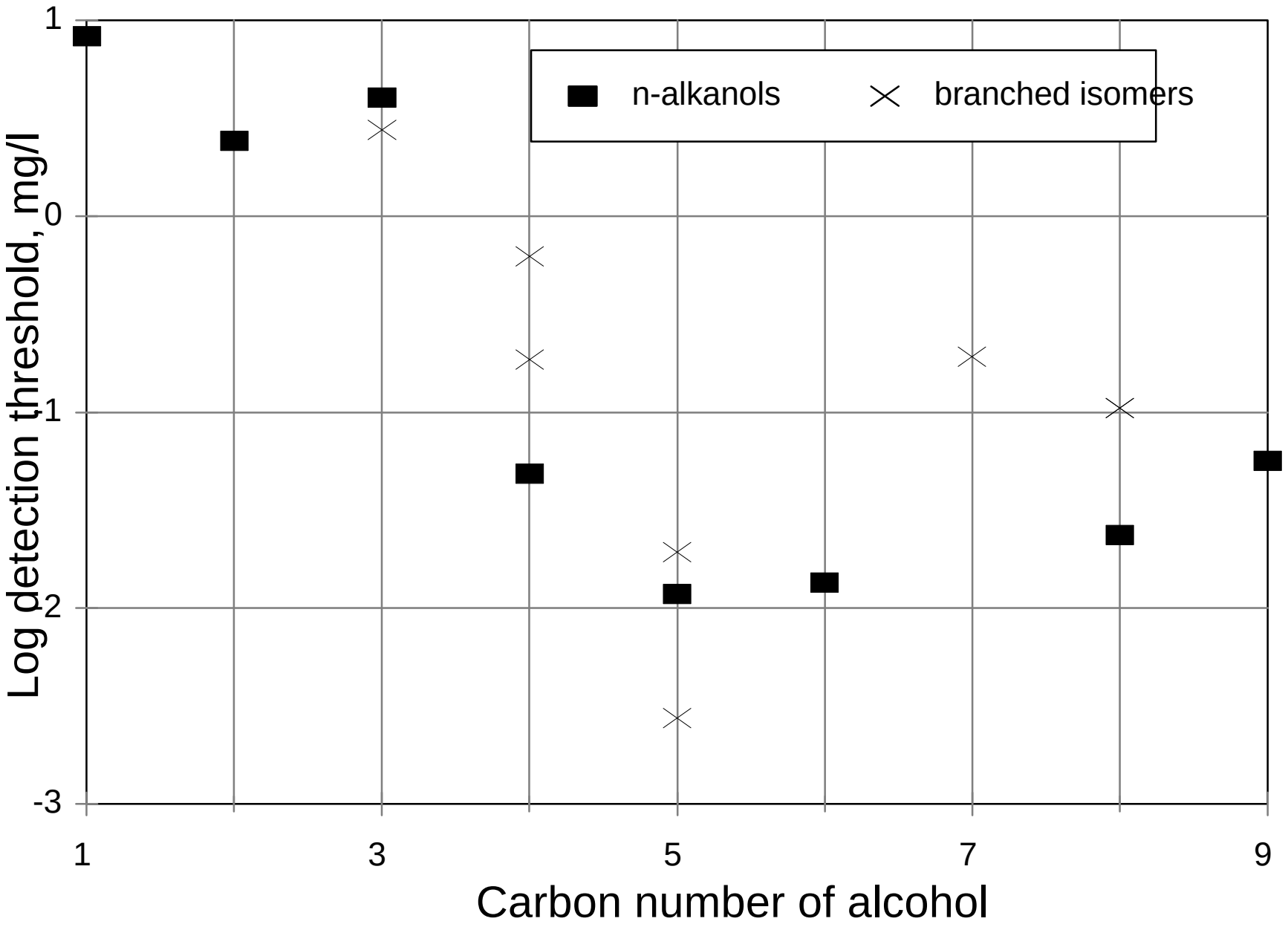

Figure 2. Odour detection thresholds of acetates in aqueous solution.